Iron K-Edge EXAFS Investigation of
Ash Deposits From Coal Combustion

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INTRODUCTION

The formation and buildup of the slag deposits on wall tubes is one of the most serious problems in pulverized coal combustion for power generation.   This phenomenon, traditionally called wall slagging, is known for its undesirable effects on heat and mass transfer.   Many empirical formulationsa based on the silica percentage and acid/base ratio have been developed in the past to describe the slag characteristics.   Unfortunately, due to variation of several factors such as flame pattern turbulence, residence time, temperature distribution, gas velocity, etc. within the boiler, these empirical formulations are of limited use in the prediction of the behavior of the slag.   In addition, these formulations do not take into consideration of the interaction between the constituents of the coal mineral matter.   Another problem in this area is the lack of information on the transition of fluid slag to a solid form and the mechanism of formation of sticky deposits.

Further work in understanding the chemical "structure" of the slags should be profitable in relating the major issue of the influence of coal mineral matter on the operational characteristics of the commercial boilers. Application of Synchrotron-Induced X-Ray Absorption Fine Structure (EXAFS) in such studies was explored and an understanding of the local structure of the iron atoms in the slags derived from a commercial boiler forms the scope of this study.

EXAFS has now become a standard tool for structural determinations.   Through EXAFS, it is possible to study the local environment of specific atomic species regardless of the physical state of the material under investigation and one could derive radial structure functions for the short range order near an absorbing element.   In simpler terms, EXAFS represents the oscillatory structure due to interference between the outgoing photoelectron wave propagating from the x-ray absorbing atom and the incoming wave backscattered by the neighboring atoms.   The EXAFS structure is observed over several hundred electron volts past the absorption edge and many excellent review articles are available on the theory and practice of EXAFS (1-4).

EXPERIMENTAL PROCEDURE

The slag samples for EXAFS analysis were taken from the upper furnace wall of the Mercer Station of Public Service Electric & Gas company, Newark, New Jersey. This is a "wet bottom" unit which means that ash is removed from the furnace bottom as molten slag. This type of furnace design is commonly used with coal which have lower fusion temperatures.

The slag deposits were derived from a Virginia Pocohontas No. 5 bituminous coal. Three samples were analyzed by EXAFS technique: (1) an ASTM ash of the original coal, (2) an inner part of the slag deposit close to the tube wall, and (3) an outer part of the deposit thought to be formed at a higher temperature. The EXAFS materials were sampled from a large block of several feet long slag deposit which was about 6-in. to 8-in. thick.

The EXAFS measurements were made at room temperature on beamline X-19A, in the National Synchrotron Light Source (NSLS), at Brookhaven National Laboratory. The X-19A beamline is equipped with a NSLS boomerang-type double-drystal fixed-exit monochromator. An Si(III) crystal with a Brag angle range of 8° to 15.5°, corresponding to an energy range of 2.12 to 7.93 keV was employed in this study. The electron energy was 2.5 GeV and the beam current was within the range of 90 to 125 mA. The vertical beam height was 0.5 mm and the energy resolution was in the order of 0.7 eV. An Fe foil, obtained from Alpha Products, Danvers, Massachusetts, was used for energy calibration, and the first inflection point in the spectra was noticed at 7111.3 eV. This value was used as energy shift in plotting the spectral data contained in this paper.

A fluorescent ionization detector was employed. The direct beam detector, in front of the sample, was filled with He gas and the ionization detector was filled with a gentle stream of Ar gas. A 6 μm thick manganese filter was used to improve the fluorescent detection.

The raw data was analyzed using EXASCAN data analysis program, originally developed at the University of Washington, Seattle, Washington, and later modified by Mark Eglington of the Unviersity of West Virginia, Morgantown, West Virginia. The principles underlying complicated EXAFS data analysis were discussed in detail by Teo (5).

RESULTS AND DISCUSSION

Figure 1(a) shows an example of the expanded version of the raw spectrum of standard α-Fe_2O_3, -100 eV to +200 eV from the first point of inflection. This spectrum is indicative of the x-ray absorption near edge structure (XANES) which contains information about the chemical environment of the absorbing element. The structure in the XANES region (-20 eV to +50 eV from the absorption edge) is believed to be due to electronic density of the states and is not caused by interference effects from backscattering.

The pre-edge feature has been assigned to a 1s -> 3d transition and the shoulder in the absorption edge, just prior to the edge crest, is considered to be due to 1s -> 4s transition. Even though the observed spectral features are explainable on the basis of electronic transitions, it has been suggested that there is a strong possibility of them to be due to "shape resonances" which are much more sensitive to the ligand geometry and coordination number (6).

Figure 1(b), (c) and (d) shows the expanded version of the raw spectra of the ASTM ash, inner deposit (FETUBA) and outer deposit (FESLAG), respectively. All of these spectra contain a clearly resolved pre-edge peak due to the 1s -> 3d transition as in the case of the standard α-Fe_2O_3.

The intensity of the pre-edge peak is typical of iron in its +3 oxidation state (Fe^{3+}). The magnitude of the intensity of 1s -> 3d transition has been correlated to the degree of the site distortion from a perfect octahedron on the basis of Mossbauer studies (7).

In comparison with the α-Fe_2O_3 spectrum, the 1s -> 4s feature was broadened out in all the samples derived from coal. All spectra clearly showed a sharp edge crest in identical position within the limits of experimental error. Since the Fe^{3+} in α-Fe_2O_3 is highly symmertrical and 6-coordinated, this may be true of the other samples investigated. However, the effect of other nearest neighbor bonding with Fe^{3+} on the XANES feature is not known at this time. Additional standards, incorporating (alkali, alkaline earth metals and Fe) -O bonding have to be evaluated.

Figure 2 shows the Fourier transforms (FT) of K^3-weighted K-edge EXAFS of Fe in the above samples without taking into consideration of the phase shift. There are two major peaks in the FT's corresponding to two different shells: the first peak at ~1.5 Å is attributed to Fe-O atom pair correlation. Considering the fact that EXAFS derived bond-lengths are accurate to 0.02 Å, there are only minor variations in the pseudo radial distribution functions (PRDF), which is representative of the actual bond length in the absence of phase shift corrections, of the samples studied. The coordination (N) of Fe by oxygen decreased to 5.0, 4.5 and 4.0, respectively, for the ASTM ash, inner deposit and outer deposit, respectively, in comparison with N = 6 for α-Fe_2O_3.

The second peak around r = 2.7 Å corresponds to Fe-Fe atom pair correlation and none of the samples from the PSE&G boiler showed intensity similar to that of α-Fe_2O_3. Furthermore, there is considerable variation in the shape of this peak. Whereas this peak was a triplet in the case of α-Fe_2O_3, ASTM ash and the inner deposit, it was a singlet in the case of the outer deposit. It appears that the nature of the deposit formed in the boiler may be related to the second peak in the FT. The shape of the peak may be correlated to the type of the neighboring atom and the intensity of the peak may be used to determine the aggregation of the Fe atoms. The inner part of the deposit, which is close to the relatively cool tube, may be expected to be enriched with volatile alkalis which condense from the gas phase and the iron from the boiler tube. In any case, the

results show that the chemical nature of iron in the boiler deposits is different from that of Fe_2O_3 and there is a continuous variation in its nature across the deposit as additional layers are formed. This characteristic feature can be employed to establish the relationship between the processing conditions and the nature of ash deposits.

CONCLUSIONS

Slagging of ash and fouling of heat exchange tubes are two major problem areas in combustion of coal and other carbonaceous feedstock containing appreciable amounts of mineral matter in it. From the results of this study, employing samples generated in a large-scale utility boiler, it appears that XANES/EXAFS can be used as a structural problem of the materials that cause slagging and fouling, in order to obtain greater insight into the mechanism of their production. The EXAFS study of several other key elements such as Na, K, Ca, Al and S will be required to obtain a clear picture of the slag formation characteristics. The results can be applied to other emerging clean coal technologies such as fluidized bed combustion, coal-fueled gas turbines, etc.

ACKNOWLEDGEMENT

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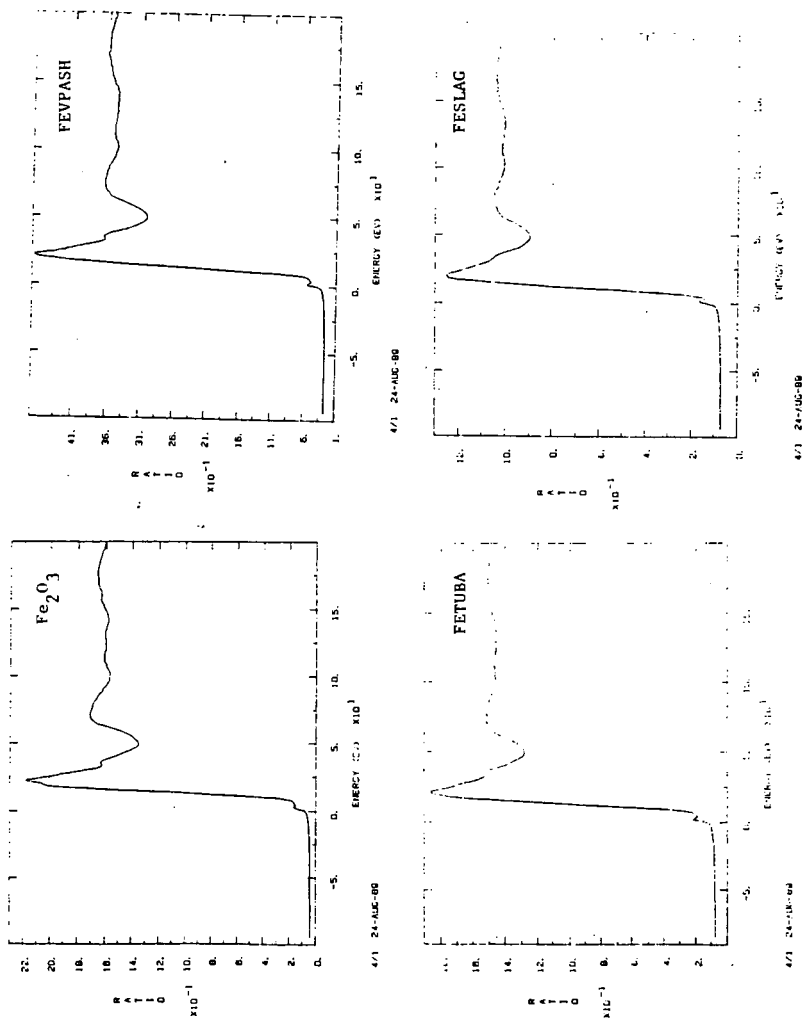7. Bancroft, G. M., Maddock, A. G. and Burns, R. G. Geochem. Cosmochem. Acta, 31, 2219 (1967).
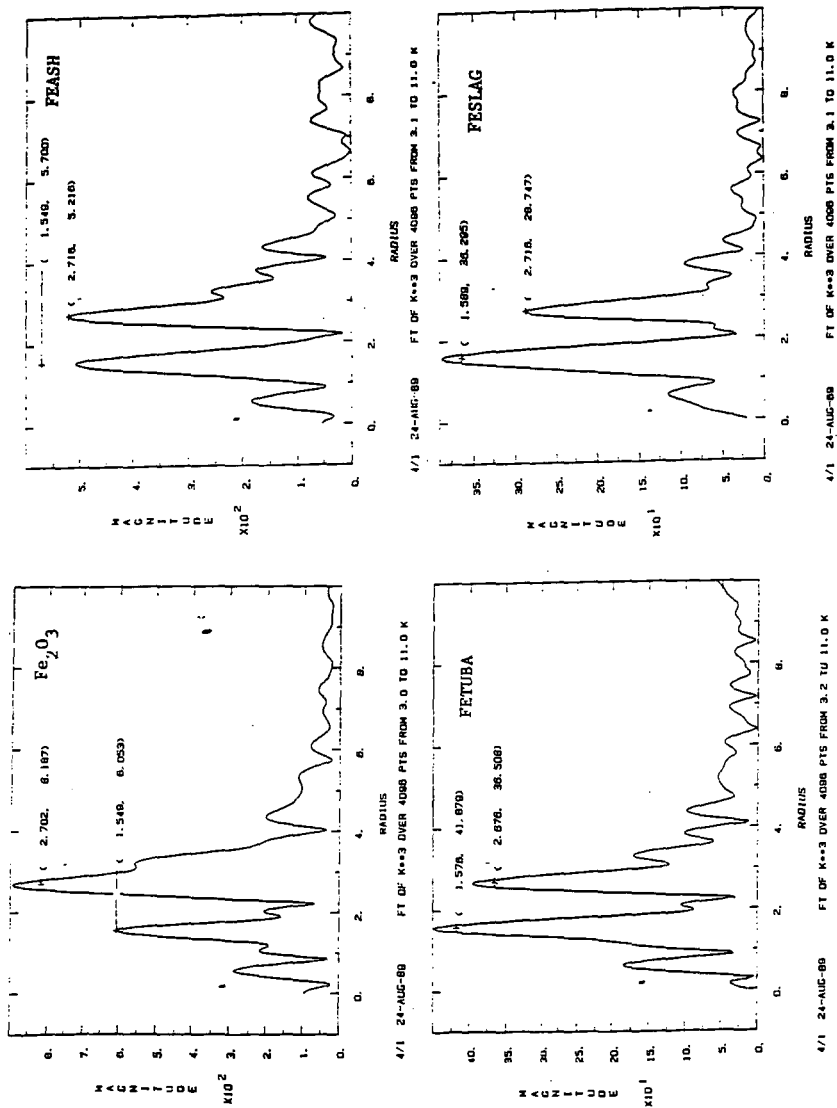
FIGURE 1. X-RAY ABSORPTION NEAR EDGE SPECTRA (IRON K EDGE)

FIGURE 2. Fe K-EDGE PSEUDO RADIAL DISTRIBUTION FUNCTIONS